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THE PROBLEMS OF PITTING IN AUSTENITIC CR-NI-STEELS

by

H. GRÄFEN

Metalloberfläche 13 No 6 (June 1959) pp 161-166

(From German)

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THE PROBLEMS OF PITTING IN AUSTENITIC Cr-Ni-STEELS

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Investigations into corrosion by "pitting" in various solutions - the effect of Redox systems, oxygen and p value - construction of Potential/Time curves and voltage curves - the effect of Nitrate additives - electrochemical properties of halogen ions - effects connected with the use of alloys - connection between "pitting" corrosion and stress cracking corrosion.

1. INTRODUCTION

Passive metals and alloys which include austenitic Cr-Ni steels, are strongly resistant to the action of many corrosive substances and are therefore frequently employed in the chemical industry. Under certain conditions, however, this type of metal is subjected to pitting corrosion. These areas are small; pitting, however, can lead rapidly to complete perforation of the material. Clearly this phenomenon represents a particularly undesirable form of corrosion, since for the same current density a localised attack will lead much more quickly to failure in a component than is the case with evenly distributed corrosion. Although to all outward appearances, pitting also occurs in non-passive metals, the process is, however, only completely characteristic in the case of passive metals and alloys. This type of corrosion is of particular interest here since it can lead to tensile crack corrosion. This frequently occurs in practice. Fig 1 illustrates the effect of pitting in a 18/8/2-Cr-Ni-Mo steel saturated in ammonium sulphate. The mother liquor

in this case contained small quantities of chloride. Fig 2 shows pitting on the surface of an 18/8 Cr-Ni steel tube attacked by ammonium chloride, which is leading to tensile crack corrosion in several places.

Pitting, as is evident from its visible effects, occurs through collapse of the inert or passive layer at certain points on the metal surface. This process leads to active-passive elements whose potential difference, as can be estimated from the following experiments, could amount to 0.5 V in stainless austenitic steel; here, however, certain theoretical difficulties arise, since this interpretation, of course, contradicts "all or nothing" law of passivity^[1]. It must therefore be accepted that the corrosion products in the holes that are formed are particularly important since they establish certain electrical conditions which lead to stabilisation of the electrode homogeneity, in particular a voltage drop and a shift in the Flade potential at the cavity base as a result of increased resistance and enrichment of acid.

With sufficient depolarisation on the cathode, the corrosion element acts strongly and can lead to rapid perforation of the anode. From these considerations it is possible to separate the pitting into two stages:

1. The formation of localised areas of activity.
2. The formation and growth of cavities up to complete rupture.

Although theoretical interpretation of the first process still presents difficulties (this will be further dealt with later), there are observations available with regard to point 2.

It has been shown that in general there is only one group of anions capable of mounting localised attacks against passive coatings. This is the halide group, with the exception of the fluorides^[2]. As a result pitting occurs in solutions containing chlorides, bromides, and iodides. Redox systems having a positive oxidation potential have a beneficial effect^[3]. Oxygen as a passivity producing or maintaining oxidising agent, and as a cathodic depolariser, has already been discussed^[3, 4].

The purpose of the following investigation was to further examine the behaviour of pitting corrosion on austenitic Cr-Ni steels.

2. EXPERIMENTS WITH HEATED SOLUTIONS AND REGISTRATION OF POTENTIAL/TIME CURVES.

Table 1 gives the results of pitting corrosion tests in 18/8 Cr-Ni steels in a 10% solution of $MgCl_2$ at 80° C, with additions of various salts. A continuous stream of air was passed through the solutions during the experiments. Iron-III-sulphate and copper sulphate were found to be particularly effective as additives. In both cases we were concerned with reducible cations having a positive potential. The $Fe^{+++} + e \rightarrow Fe^{++}$ reaction yields a normal potential of 0.77 volts and $Cu^{++} + e \rightarrow Cu^+$ a potential of 0.17 volts (referred to monomolecular solutions). In considering these data it must be borne in mind that hydrolysis of the Iron-III-salt renders that particular solution strongly acid (p_H approximately 1-2), so that only the strong oxidising effect of the Redox system can produce the equilibrium potential which makes pitting possible. In the case of the less acid solution with added $CuSO_4$ the appreciably lower oxidation potential nevertheless suffices to bring about pitting. At the same time these Redox systems naturally behave as strong cathodic depolarisers and thereby hasten the pitting process. If a Chromium-III-salt, (eg $CrCl_3$) is added to the $MgCl_2$ solution the steel sample becomes active and dissolves. The trivalent chromium has an oxidising potential of - 0.41 volts and is thus definitely a reducing agent.

Redox systems with reducible anions do not influence the rate of pitting to any great extent. Even definite passivators, such as nitrates and bichromates, have scarcely any effect in concentration such as those used in these experiments. Fig 3 shows the assembled Potential/Time curves for the $MgCl_2$ experiments (Table 1). In the case of the pure $MgCl_2$ solution 18/8 Cr-Ni-steel potential slowly increases. Here the only available oxidising agent is atmospheric oxygen.

In this case the test sample reaches a potential of approximately 0 mV Eh and there is extremely little pitting; what there is is mostly confined to the edges. In approximately neutral solutions containing chloride, pitting does not occur until a certain potential is exceeded. This potential is dependent on the concentration of Cl⁻ ions, and on the p_H value. Fig 4 (taken from M. Pourbaix ^[5]) gives the current-voltage curve of an 18/8 Cr-Ni steel in an acetate buffer (p_H = 4.9) with and without added chloride. In this instance pitting sets in when the potential exceeds 600 mV Eh. This point can be denoted as the pitting potential. When pitting starts there is an initial falling off in potential. This is a consequence of the corrosion mixed potential which has now arisen, which exhibits certain fluctuations. This development is accompanied by a noticeable rise in electrical current. As the p_H value diminishes (with increased acidity) and the chloride content increases, there is a shift in pitting potential: a shift to more negative potential values. This means that as solutions become more acid (p_H = 1-2) the difference between Flade potential and pitting potential is extremely small.

It can be seen from the above that with almost neutral chloride solutions, pitting can only occur in the presence of an oxidising agent capable of raising the equilibrium potential of the steel to the level of the pitting potential. This also explains why, under certain conditions, no corrosive attacks take place in boiling solutions, which have little atmospheric oxygen dissolved in them. This oxygen, it will be recalled, acts as the oxidising agent. At lower temperatures, on the other hand, corrosion certainly does occur. As the temperature rises the concentration of dissolved O₂ diminishes and is at its lowest when the solution reaches boiling point.

Table 2 shows the results of a number of experiments in the course of which 18/8 Cr-Ni steel was boiled or heated in FeCl₃ solutions. The object of these tests was to investigate the effect of temperature,

concentration, atmospheric oxygen, the p_H value and of various passivating additives. If air is passed through a 10% solution of $FeCl_3$ at $30^\circ C$ pronounced pitting is observable; with a similar solution at boiling point pitting occurs at the early stages, but subsequently the specimen becomes slowly activated and the corrosive attack is distributed to an increasing extent over the whole surface of the metal. With a 5% $FeCl_3$ solution there is pronounced pitting at boiling point, as well as at lower temperatures. The "pits" in this case are tiny but very numerous. When the concentration of chlorine ions increases and the p_H value reduces, the quantity of O_2 necessary to maintain residual passivity is also greater, so that in a boiling solution, under certain circumstances, (the concentration of dissolved oxygen being less) complete activation can set in. When oxygen is instituted, pitting does not occur unless there is anodic polarisation. If the p_H value of the acid hydrolysing iron chloride solution is raised to about 6, by addition of alkalis, the rate of pitting decreases appreciably. When it was raised above 7 no pitting was observed.

Fig 5 illustrates a number of potential/time curves corresponding to the experiments described above. The activation of 18/8 Cr-Ni steel test samples in a boiling 10% solution of $FeCl_3$ (owing to lack of O_2) can be recognised by the pronounced decrease in potential, although pitting corrosion has already occurred at the corresponding positive potentials. As the free hydrochloric acid is neutralised, the potential reduces down to negative values. Thus corrosion is considerably suppressed and can only be observed occasionally on the edges, which is probably due to the roughness of the edge.

3. CURRENT-VOLTAGE CURVES

As an extension to this investigation, particularly into the electrochemical aspect of pitting corrosion, a number of current-voltage curves were recorded. Fig 6 illustrates a typical curve for a 18/8 Cr-Ni steel

in 0.1 n H_2SO_4 at boiling point and with aeration. It can be seen that this is a case of a metastable passive system since both an active and a passive equilibrium potential are shown in the curve, denoted in the figure by R_a and R_p respectively. If a quantity of 0.5% NaCl is added and a new current-voltage curve is recorded, although both active and passive equilibrium potentials are still present, R_p shifts towards a more negative potential. With anodic polarisation the current density increases rapidly without a limiting current being established in the passive region, as is usual and can be seen even in the curves for pure H_2SO_4 . With a further addition of NaCl (the current-voltage curve for 10% is shown), the passive equilibrium potential completely vanishes. At R_a the 18/8 Cr-Ni steel is completely active in all cases, i.e. no pitting corrosion but only complete dissolution occurs. With low chloride contents, when, of course, a passive equilibrium potential exists, the steel is subjected to pitting corrosion at this potential. If R_p vanishes (with higher chloride content), then pitting corrosion can only occur by anodic polarisation. It will be clear from the above that a Redox system with positive oxidation potential can establish extraordinarily favourable conditions for the growth of pitting, as has been clearly demonstrated by the simple boiling experiments. Fig 7 shows two current-voltage curves for 18/8 Cr-Ni steel in a 10% Iron III chloride solution with air passed through it. At 50°C the rest potential is + 190 mV. At the boiling point of the solution the rest potential became - 5 mV. At + 190 mV, the steel test sample very quickly develops heavy pitting. When the solution is at boiling point, the steel becomes active, and only becomes pitted when anodially polarised.

This shows then that pitting can only occur when the potential of the steel in the solution attacking it is higher than the Flade potential, i.e. when the potential of the steel lies within a range where the steel would be passive were it not for the presence of halides, and where the so-called pitting corrosion potential is exceeded; this latter factor, however, only assumes real importance when the halide solution is

comparatively neutral. In the case of the acid solutions used in the experiments under discussion, this pitting corrosion potential lies very close to the Flade potential. We have already mentioned this fact. The shift in the rest potential to an "active" direction when solutions boil is to be explained by the collapse of the residual passive skin, which acts as a cathode, owing to lack of oxygen.

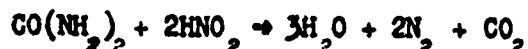
We must now consider a number of phenomena which occur when oxidising media act on austenitic Cr-Ni steels in acid solutions, producing various degrees of pitting corrosion. If reducible cations such as Fe^{+++} or Cu^{++} ions, for example, are present, rest potentials falling within the inert sphere can be set up, in conjunction with participating atmospheric oxygen, even in solutions with a low p_{H} value. If halides are present, there is localised activation. By virtue of their ability to live off electrons, halides also function as potent cathodic depolarisers, and since atmospheric oxygen has the capacity to re-oxidise the Fe^{++} ions, for example, which have been formed, a Redox system of this sort never loses its efficiency. Reducible anions on the other hand will scarcely be in a position to exercise any depolarising effect on the cathode; owing to the absence of electrostatic attraction. Thus in general the anions of oxygen acids even have a polarising effect and can be classified as inhibitors. If, for instance, nitrates are added to solutions which normally promote pitting, and providing such additives are in sufficient quantities, the corrosive attack may be checked, [3, 4]. The appearance of the nitrate ion as a reduction product is doubtless of importance in the reaction. The good inhibitory qualities of this ion are already known. Moreover the oxygen released in the process is useful for maintaining passivity. If the effect of added nitrates to 5% boiling and aerated FeCl_3 solutions, is studied with the aid of current-voltage curves on the pit-corrosive behaviour of 18/8 Cr-Ni steels in contact with such a solution, a number of interesting results are obtained which are

assembled in Fig 8. If the added NaNO_3 is only 1%, the current-voltage curve remains very similar in character to the curve for FeCl_3 solution without added nitrate. The rest potential of + 160 mV indicates pitting in the steel. The curve obtained when 5% NaNO_3 is added possesses an active (with reference to pitting) and also a passive rest potential. When anodic polarisation is present, the marginal current in its passive condition is two powers of ten higher than when the sample is in a state of normal passivity in solutions which do not contain halides.

The slight residual corrosion in passive conditions is attributable to a gradual dissolution of the inert (or passive) "skin" in the electrolyte [6], whereby a current density of approximately 10^{-6} to 10^{-5} A/cm² is observed. In solutions containing halides, this residual current is at a much higher level. Even when the residual current is normal, an anodic current density must exist, in order to conserve passivity, which causes the formation of a passive film. With solutions containing halides it will be clear that an appreciably larger anodic current is required. In the presence of chlorine ions only the inhibiting and oxidising action of comparatively high nitrate concentrations can effectively maintain passivity. Indeed stable passivity is not achieved even when the concentration is increased to 8%. In neutral halide salt solutions on the other hand, weak nitrate concentrations are sufficient to bring about a passive condition which will prevent pitting. In practice therefore we may conclude as follows: austenitic Cr-Ni steels in neutral solutions can be reasonably well protected against pitting; in acid solutions protection is difficult. It is true that, given adequate quantities of nitrate, a passive rest potential will be set up when an 18/8 Cr-Ni test sample is immersed in an acid solution containing a halide. If, however, there is subsequent activation from whatever source, the sample will develop pitting and intrinsic auto-passivation will not recur.

If urea is added to solutions containing nitrate, the corrosion-inhibiting effect of the additive again disappears. The urea reacts

as follows:



ie the nitrite (produced from the nitrate by reduction) is immediately taken up and eliminated. It is thus apparent that the inhibitive effect is to be attributed largely to the nitrite (Fig 9).

The experimental results so far described represent a valuable aid to the investigation of damage caused by pitting. Fig 1 showed a corroded ammonium sulphate saturator made of Cr-Ni-Mo steel. This had been operating for some time and had shown no sign of attack. It had then suddenly developed pitting. The attacking solution in this case was slightly acid and contained some nitrate in addition to small quantities of chloride. We have now seen from the current-voltage curves that the protective action of nitrates in acid solutions does not lead to stable passivity. We must therefore conjecture that in the above case there was a sudden localised activation, due perhaps to a temporary rise in the chloride level. It was indeed confirmed that there had been such a rise. Even after re-establishment of normal analytical values, the pitting process continues.

Fig 10 shows an 18/8 Cr-Ni tube which was destroyed extremely rapidly by the action of an acid solution containing copper sulphate, iron sulphate, cobalt sulphate and minimal quantities of chlorides.

4. THE EFFECT OF HALOGEN IONS ON INERT METALLIC SKINS

We are already in a position to make a number of positive statements about the mechanism of pit-corrosion. There is one phenomenon however which is hard to explain: the action of the halogen ions. How precisely are these ions able to annul the effects of polarisation? How, specifically, can they, in small concentrations, raise the marginal current in the inert zone? How do they achieve their localised breakthroughs in inert skins?

Here, quite clearly, we are concerned with electrochemical occurrences within the Helmholtz Double Layer. According to Nernst and Helmholtz, a layer of positive ions marks the boundary, so to speak, between the electrolyte

and the cathode. Within and throughout the electrolyte, however, there is an equal distribution of anions and cations. On the cathode side there is a thin deposit of electrons. We should add that, according to later conceptions, this condenser-like double layer is not only composed of cations on the electrolyte side; despite the negative charge on the cathode, it can also include anions. In addition, it can incorporate undissociated molecules possessed of dipole characteristics, also colloids and other particles moved or directed by the electrical field. The structure of the Double Layer is determined not only by electrostatic attraction but also by adsorptive forces. This applies particularly to the anions.

According to Grahame [7], anions can establish direct contact with metallic surfaces, a capacity which is dependent on their permanent and induced electrical moment, dependent especially, that is to say, on their "deformability" - or distortion. The anions most readily distorted are those of chlorine, bromine and iodine. They might therefore be expected to lend themselves more easily to adsorptive connexion (Van der Waals style) with metallic surfaces.

Cathodic deposition in metals involves two distinct groups of anions; first, those whose effect on the metal excess voltage is either a reduction or non-existent; secondly, those which invariably increase the voltage. The first group, known as the activating anions, includes all halides except the fluorine ion. All other anions belong to the second group [8].

Thus the halides occupy a special position in which the anomalous behaviour of the fluorides is particularly noticeable. This was also evident in our experiments concerned with factors affecting passivity in austenitic Cr-Ni steels [2], and in our investigations into tear corrosion [9], and pitting. It follows that when passive metals and alloys are locally activated, there is a possibility that, because distortion takes place easily, the halide ions will penetrate the double layer and that in particular areas of the oxide or oxygen skin a mutual reaction will occur

in the course of which the oxygen becomes replaced, and easily soluble salts are formed. The particular areas could arise in the passive skin through lattice distortion or through constructional flaws occasioned by the metallic surface e.g. the effects of granular boundaries, displacements, dislocations, inclusions and the like. Thus roughly finished surfaces are notably more susceptible to pitting than polished surfaces.

5. THE EFFECT OF ALLOY CONSTITUENTS AND PROCESSES

It will be seen that the tendency of a stainless, austenitic Cr-Ni steel to develop pit corrosion is not only dependent on its corrosive surroundings but also on the quality of the passive skin. The factors which influence the process are surface treatment, heat treatment, malformation, roll texture, alloy constituents and, on occasion, passivation treatment.

The favourable effect of surface polish has already been mentioned. Any form of heat treatment which produces a smooth, homogeneous, flakeless structure reduces liability to pitting. Austenitic-stabilising additives such as nitrogen naturally have a similar tendency.

Other alloy constituents can increase the resistance of the metal to pitting. We have often described the beneficial effect of molybdenum, which is in any case well known.

Streicher ^[4], however, has shown that the effect of Mo only comes into play under conditions of chemical passivation. Moreover, when the attack is by bromine ions no effect of Mo is observed. With chlorine ions the effect is present. Silicon also has a favourable effect. Rhodin's researches ^[10], showed that the silicon concentration is greater in the passive layer than elsewhere.

In general we may say that any improvement in the passive layer tends towards increased resistance to pitting; this improvement could take the form of a reduction in the number of faults in the skin which are influenced by the surface of the steel; or it could be due to an improvement in the chemical stability of the metal.

6. THE APPEARANCE OF PITTING AND ITS RELATIONSHIP TO STRESS CRACKING

The forms in which pitting occurs are various. In the presence of chlorine ions for instance, inert iron will normally develop circular, hemispherical and fairly smooth cavities. With the austenitic Cr-Ni steels however we get an impression of jagged and irregular orifices and indentations. If we make transverse cuts at right angles to the surface of the metal we can normally expect to find that the cavity undermines the surface in a sideways, as well as a downward, direction. This phenomenon is well illustrated in Fig 11. Sometimes in places only pinprick holes are visible but these conceal extensive excavation below the surface.. Elsewhere separate small pitted localities may grow together into nests or colonies.

Another type of selective corrosion in austenitic Cr-Ni steels is so-called stress cracking. Stress cracking is also prompted by the action of halides on occasions when (as the name suggests) the metal is subject to residual or tensile stresses. In both cases, ie. with both pitting and crack formation, the process of electrochemical decomposition is initiated by localised activation; in both cases also, the active anodes are small with respect to passive cathode.

We might therefore assume certain relationships between the two forms of corrosion. We shall now briefly expound this relationship in the light of a number of experiments which have been carried out.

A 42% solution of $MgCl_2$ at boiling point is normally used as the test solution for transcrystalline tear corrosion in austenitic steels. Tensile test pieces of these steels which are stressed in this solution in the presence of atmospheric air, rupture in a comparatively short time. As the $MgCl_2$ is diluted, so the resistance of these stressed test samples to corrosion of this sort increases. There comes a point where break-up

no longer occurs at all. Thus sample bars of 16/13 Cr-Ni steel were (in one experiment) treated for 1,200 hours with a boiling 10% solution of MgCl_2 under normal atmospheric conditions; immediately afterwards they were exposed to the solution for a further 1,000 hours, air being passed through the whole time. There was no corrosion whatsoever. If however 0.1% FeCl_3 - an oxidising agent - is added to the solution, both crack formation and pit corrosion occur after some time, (in the present experiment the time-lag was 10 days). This is illustrated in Fig 12 and 13. By adding acid, moreover, it is possible to initiate crack formation even in solutions containing only small quantities of Chloride. These observations indicate that, as in the case of pit corrosion, a marginal potential must be reached and exceeded before the corrosive process is initiated and that, as the concentration of hydrogen ions increases, this marginal potential likewise decreases to more negative values. Comparative investigations have now shown that when conditions of attack are identical the two marginal potentials - pitting potential and crack potential - are almost identical. It will be seen therefore that in both cases we are concerned in fact with a marginal potential due to selective activation by hydrogen ions. The passivations can be accounted for by the tensile strain to which the metal is subjected. This stress creates additional flaws in the inert skin and this in turn results in reduced localised halide activation. This leads to a slight shift of the marginal potential in a negative direction.

Whether, after selective activation, cracks or pits develop, depends not only on the presence of stresses but also to a considerable extent on the nature of the attacking medium. Thus with a 10% FeCl_3 solution at 80° only pitting occurs and this is the case even in samples under high tension. When the quantities of reducible Fe^{+++} ions are small, both types of corrosion occur. If only oxygen is available as

a depolariser, crack corrosion preponderates. The particular corrosive manifestation is clearly dependent on the state of the cathode. If electrons are consumed on the cathode at great speed, holes arise so rapidly that cracks never get a chance to develop. If however there is a slow reaction on the cathode, the situation is favourable to the formation of cracks. Close observation of the metallic surface then reveals tiny dot-like corroded patches which in fact are the beginnings of cracks i.e. of crack corrosion. There are of course transitional forms as well.

SUMMARY

Passive metals and alloys due to their resistance to corrosion are widely used. In the chemical industry stainless austenitic Cr-Ni steels are particularly favoured. Unfortunately even these alloys, like all inert metals are subject to 'pitting' under certain conditions.

The development of this type of corrosion can be divided into two stages:

1. The initiation of localised attack
2. The formation and growth of cavities.

An attempt is made, on the basis of several experiments, to obtain further information concerning pitting in Cr-Ni steels. Experiments were in fact carried out by immersion of 18/8 Cr-Ni steels in heated solutions and recording the current/voltage curves together with voltage/time curves. The solutions used were various, but the majority had a low p_H value.

Solutions which are strongly conducive to pit corrosion are those which contain halides (other than fluorine) in conjunction with Redox systems with reducible cations, the latter being also active as depolarisers. In acid solutions in which 18/8 Cr-Ni steel would normally become active, pitting can only be induced by anodic polarisation or by the addition of Redox systems. Furthermore, sufficient oxygen must be present to maintain the passivity of the cathode. Alkaline

inhibit pitting.

If nitrates are added in sufficiently high concentrations, pitting in neutral halide solutions is prevented, since 18/8 steel test samples become passive. In acid solutions however the addition of nitrates gives rise to metastable passive rest potentials.

An explanation is given of the special electrochemical characteristics of halogen ions, which are of significance in connexion with select activation of inert metals. Our study also touches on the influence of anion alloys on pit corrosion and on the relationship between pitting and crack corrosion.

FIGURES AND DIAGRAMS

- FIGURE 1 Pitting on the interior wall of an Ammonium Sulphate saturator made of 18/8/2 Cr Ni Mo steel.
- FIGURE 2 Pitting with transition in places to crack corrosion on an 18/8 Cr Ni tube.
- FIGURE 3 Current-voltage curves for 18/8 Cr Ni steel in various solutions at a temperature of 80° C/Air.
- Sichtbarer Lockfrassung = visible pitting
Probe aktiv = sample active
- FIGURE 4 Current-voltage for an 18/8 Cr Ni steel in an acetate buffer ($p_H = 4.9$) with and without added NaCl (Pombaix method).
- FIGURE 5 Potential/Time curves for 18/8 Cr Ni steel in a boiling $FeCl_3$ solution.
- FIGURE 6 Current-voltage curves for 18/8 Cr Ni steel in H_2SO_4 and NaCl solutions.
- $\frac{n}{10} H_2SO_4$, boiling
- - - - $\frac{n}{10} H_2SO_4 + 0.5\% NaCl$, boiling
— · — $\frac{n}{10} H_2SO_4 + NaCl$, boiling
- Stromdichte in Amp/cm² = Current density in amps/cm².
- FIGURE 7 Current-voltage curves for 18/8 Cr Ni steel in 10% $FeCl_3$ solution.
- 10% $FeCl_3$ /50°/air
- - - - 10% $FeCl_3$ /boiling/air.
- FIGURE 8 Current-voltage curves for 18/8 Cr Ni steel in boiling $FeCl_3$ and $NaNO_3$ solutions.
- FIGURE 9 The influence of urea on the anti-pitting effect of an $NaNO_3$ additive.
- FIGURE 10 Damaged tube of 18/8 Cr Ni steel.
- FIGURE 11 The form in which pitting develops.
- FIGURE 12 Simultaneous appearances of pitting and crack corrosion.
- FIGURE 13 Sectional view of the sample in Figure 12.

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SOLUTION	TEMPERATURE IN °C	LENGTH OF EXPERIMENT IN DAYS	EXTENT OF CORROSION OBSERVED
10% MgCl_2 + air	80	8	A few small pitted areas
10% MgCl_2 + 3% NaNO_3 air	80	8	A few small pitted areas
10% MgCl_2 + 3% $\text{K}_2\text{Cr}_2\text{O}_7$ air	80	8	A few small pitted areas
10% MgCl_2 + 3% $\text{Fe}_2(\text{SO}_4)_3$ air	80	2	Extensive pitting but increasing activation
10% MgCl_2 + 3% CuSO_4 air	80	2	Extensive pitting
10% MgCl_2 + 3% CrCl_2 + air	80	8	Test samples completely active Dissolution

Table 1 Experiments with 18/8 Cr Ni steel in various heated MgCl_2 solutions.

SOLUTION	TEMPERATURE IN °C	LENGTH OF EXPERIMENT IN DAYS	EXTENT OF CORROSION OBSERVED
5% FeCl ₃ air	80	6	Pronounced pitting after 4 days
10% FeCl ₃ air	80	4	Considerable pitting
5% FeCl ₃ air	Boiling	6	Numerous small holes after 4 days
10% FeCl ₃ air	Boiling	4	Some pitting in the beginning followed by increasing activation
10% FeCl ₃ nitrogen	Boiling	6	No pitting Dissolution Test samples active
10% FeCl ₃ + HCl pH ~ 1.0 air	Boiling	4	Samples completely active Dissolution
10% FeCl ₃ + NaOH pH ~ 6.0 air	Boiling	16	Slight pitting on out surfaces only
10% FeCl ₃ + 3% NaNO ₃ air	80	2	Numerous tiny holes
10% FeCl ₃ + 10% NaNO ₃ air	Boiling	6	No pitting Covering layer (Deckshicht) visible on samples.

Table 2 Experiments in boiling 18/8 Cr Ni steel in various FeCl₃ solutions.

Bild 1: Lochfraß an der Innenwand eines Ammoniumsulfatlagers aus 18/8 CrNi-Stahl

Bild 2: Lochfraß mit Übergang zu Spannungsrisskorrosion an einer 18/8 CrNi-Stahlschraube

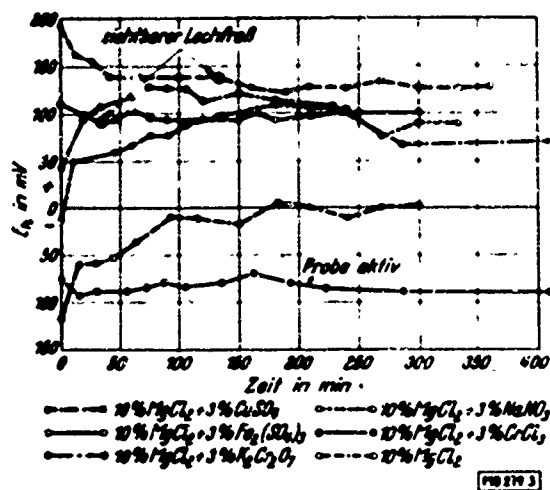


Bild 3: Potential-Zeit-Kurve von 18/8 CrNi Stahl in verschiedenen Lösungen bei 80°C/Luft

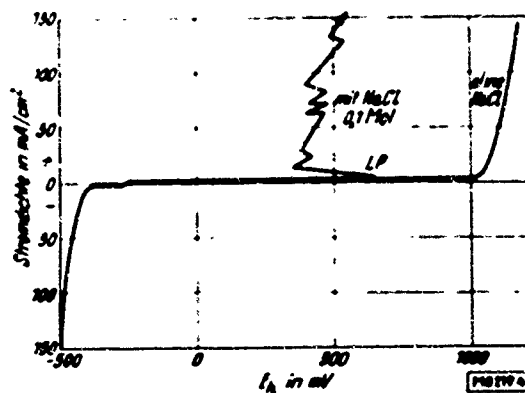


Bild 4: Strom-Spannungs-Kurve eines 18/8 CrNi-Stahles in Acetatpuffer (pH = 4,9) mit und ohne NaCl-Zusatz (nach Pourbaix)

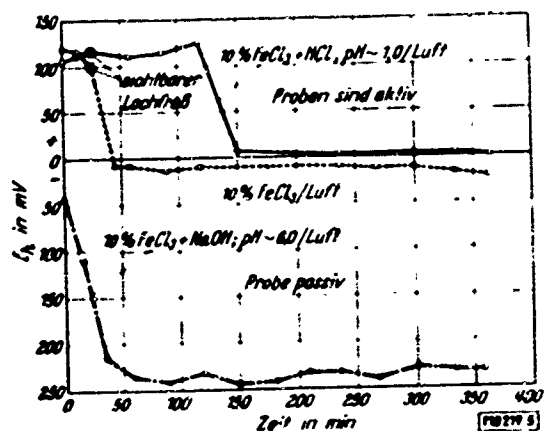


Bild 5: Potential-Zeit-Kurven von 18/8 CrNi Stahl in siedender FeCl3-Lösung

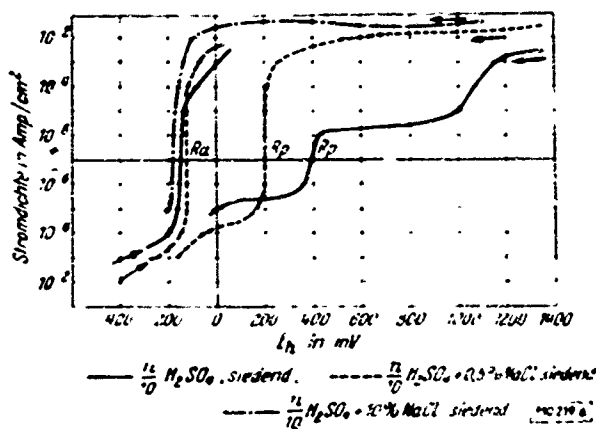


Bild 6: Strom-Spannungs-Kurven von 18/8 CrNi Stahl in H2SO4 und NaCl-haltigen Lösungen

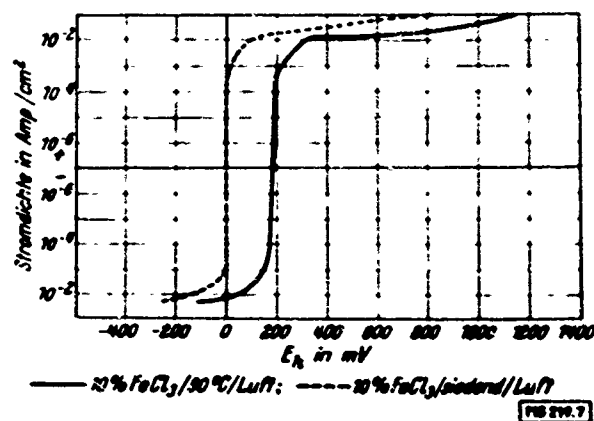


Bild 7: Strom-Spannungs-Kurven von 18/8 CrNi Stahl in 10% FeCl3-Lösung

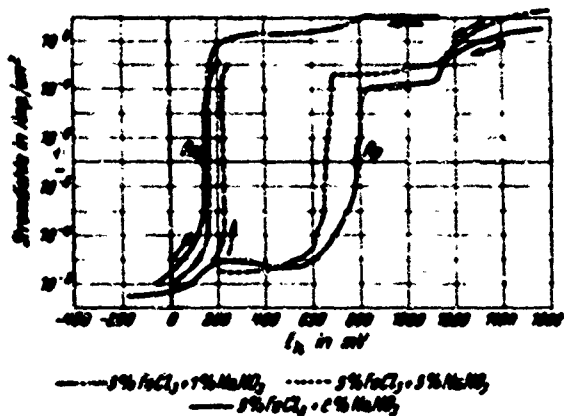


Bild 8. Strom-Spannungs-Kurven von 18.8 CrNi Stahl in saurem, FeCl₃ und NaNO₂ enthaltenden Lösungen

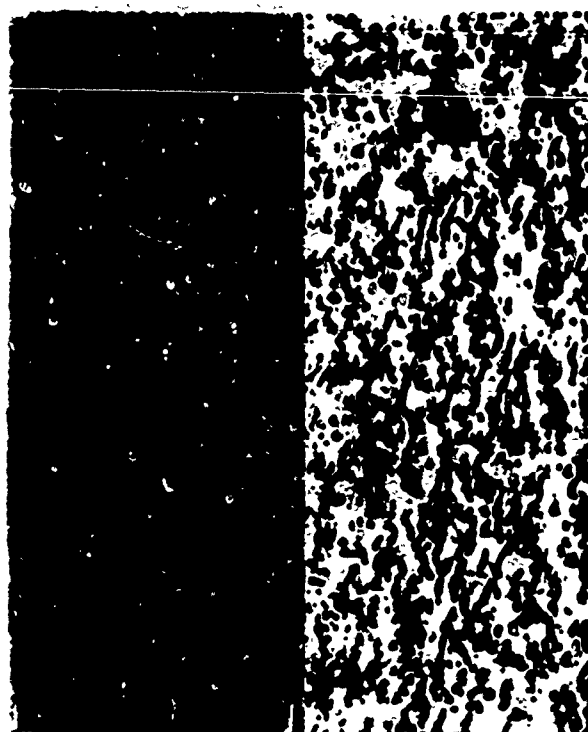


Bild 9. Einfluß von Harnstoff auf die korrosionsverhindernde Wirkung eines NaNO₂ Zusatzes



Bild 10. Zerstörte Rohrschlinge aus 18.8 CrNi Stahl



Bild 11. Ausbildungsforn des Lochfraßes



Bild 12. Gleichzeitiges Auftreten von Lochfraß und Spannungsrisskorrosion



Bild 13. Querschnittsaufnahme zu Bild 12